

Estimating Cenozoic ice volume from deep-sea records

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Summary The purpose of this guide is to provide a background on the use and application of oxygen isotopic and Mg/Ca ratio chemostratigraphy in understanding ice volume changes at high latitudes. This will include the uncertainties involved and possible causes for errors in constraining ice volume.

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Introduction

The use of geochemical records from deep-sea sites has been an important means of constraining ocean temperatures and ice volume at the poles (e.g., Shackleton and Kennett, 1975; Miller et al., 1987; 1991; Zachos et al., 2001). Because calcium carbonate incorporates the oxygen isotopic composition of the seawater, both calcareous macro and microfossils (e.g., foraminifers) have been used to estimate seawater temperature, and more importantly for this chapter, ice volume during time intervals that significant ice sheets existed (Miller et al., 1985; 1987; 1991; Wright and Miller, 1992; Zachos et al., 2001). However, because $\delta^{18}\text{O}$ values are a function of the temperature during calcification and the $\delta^{18}\text{O}$ value of the seawater (which is primarily controlled by ice volume), methods have been developed in an attempt to isolate the ice volume signal. This includes comparing $\delta^{18}\text{O}$ records from planktonic foraminifers from western tropical equatorial sites and benthic foraminifers to estimate the ice volume signal in the $\delta^{18}\text{O}$ of seawater and calibrating $\delta^{18}\text{O}$ records to eustatic records from backstripped stratigraphy from passive continental margins. In recent years, great advances have been made to demonstrate that Mg/Ca ratios can provide a means to isolate seawater temperatures, permitting determination of the $\delta^{18}\text{O}$ of seawater ($\delta\omega$) and therefore provide constraints on ice volume. The purpose of this chapter is to provide a brief summary on these methods that use distal records from deep-sea sites to place constraints on the evolution of the cryosphere during the Cenozoic.

The oxygen isotope paleothermometry

Three isotopes of oxygen exist, of which ^{16}O is by far the most common (99.759%), followed by ^{18}O (0.204%), with ^{17}O being the most rare (0.037%). Of these isotopes, ^{16}O and ^{18}O are used for paleotemperature estimates based on their abundance. Paleotemperature and ice volume estimates from $\delta^{18}\text{O}$ are result of isotopic fractionation (Urey, 1947 Epstein et al., 1953). Fractionation is due to the slightly different physiochemical properties each isotope has owing to different atomic masses, which results in differences in the velocities of isotopic molecules of the same compound (i.e., vibrational energy). The difference in vibrational energy is the dominant source of isotopic fraction. At high temperatures, the equilibrium constant for isotopic exchange tends to be similar, because small differences in mass are less important when all molecules have very high kinetic and vibrational energies.

The ‘normal’ ratio of $^{18}\text{O}/^{16}\text{O}$ is about 400; therefore, variations of this ratio are usually multiplied by a large number (1000), so the values are small whole numbers. Oxygen isotope ratios ($\delta^{18}\text{O}$) are expressed as the difference from a standard (‰) (Equation 1). This is done because it is difficult to measure absolute ratios owing to the variable fractionation within the mass spectrometer. This standard can be from a sample of calcium carbonate (e.g., lab standards, Bahamas oolite, Solenhofen limestone) that has a constant value or to seawater (e.g., SMOW = Standard Mean Ocean Water).

$$\delta^{18}\text{O} = \left[\frac{(^{18}\text{O}/^{16}\text{O})_{\text{spI}} - (^{18}\text{O}/^{16}\text{O})_{\text{SMOW}}}{(^{18}\text{O}/^{16}\text{O})_{\text{SMOW}}} \right] \times 10^3$$

Equation 1.

If $\delta > 0$, this means that the sample is enriched in the heavy isotope relative to a standard.

If $\delta < 0$, this means that the sample is depleted in the heavy isotope relative to a standard.

Isotope fractionation in the hydrosphere and atmosphere

As evaporation of surface water occurs, the H_2O vapor becomes depleted in ^{18}O compared to seawater. This isotopic fractionation during evaporation is temperature dependent as shown in figure 1. This ‘light water’ (water depleted in ^{18}O) that is evaporated at low latitudes is transported into the higher latitudes. With each precipitation event, the remaining water vapor becomes more depleted. Isotopic fractionation that occurs during condensation of water vapor can be described by Rayleigh Distillation (Figure 2), where at a given percent of water vapor remaining in the atmosphere, the condensed liquid will be heavier than the remaining vapor. This effect is especially significant over

continents because the water vapor cannot get recharged with the lighter isotope from evaporation (Figure 3). At increasing latitude and altitude, the remaining vapors become increasingly enriched in ¹⁶O as more ¹⁸O precipitate out.

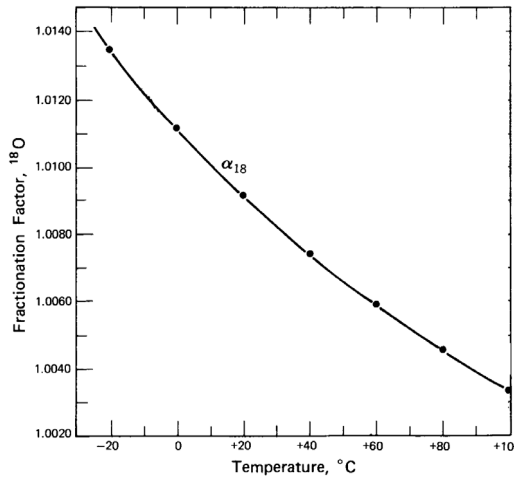


Figure 1. Equilibrium fractionation factor of ¹⁸O (α₁₈) between the vapor and liquid water phases as a function of temperature. The fractionation factor for ¹⁸O is defined as the ratio of ¹⁸O/¹⁶O in the liquid to ¹⁸O/¹⁶O in water vapor in equilibrium with the liquid. Adapted from Dansgaard (1964).

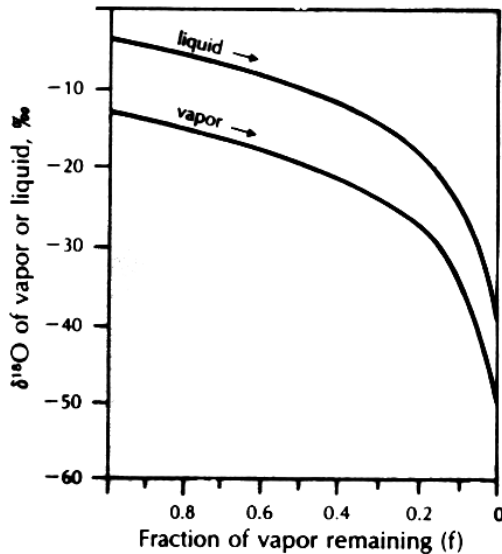


Figure 2. Effect of Rayleigh distillation on the δ¹⁸O value of water vapor remaining in the air mass and of meteoric precipitation falling from it at a constant temperature of 25°C. Adapted from Dansgaard (1964).

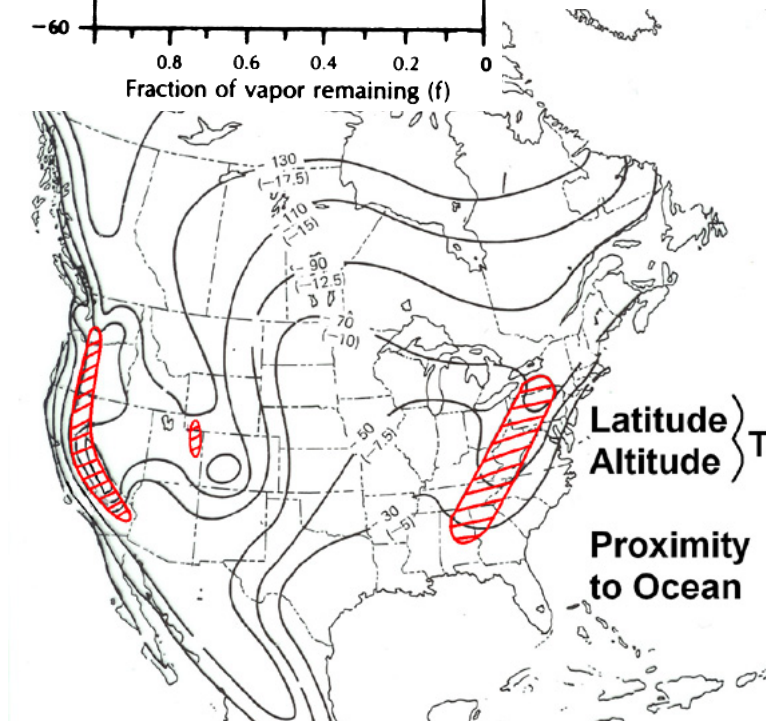


Figure 3. This shows the distribution of δD and corresponding δ¹⁸O (in parentheses) in meteoric waters in North America. Note how isotopic values deviate over areas of higher terrain (red shaded areas) as well as with proximity to the ocean. Adapted from Dansgaard (1964).

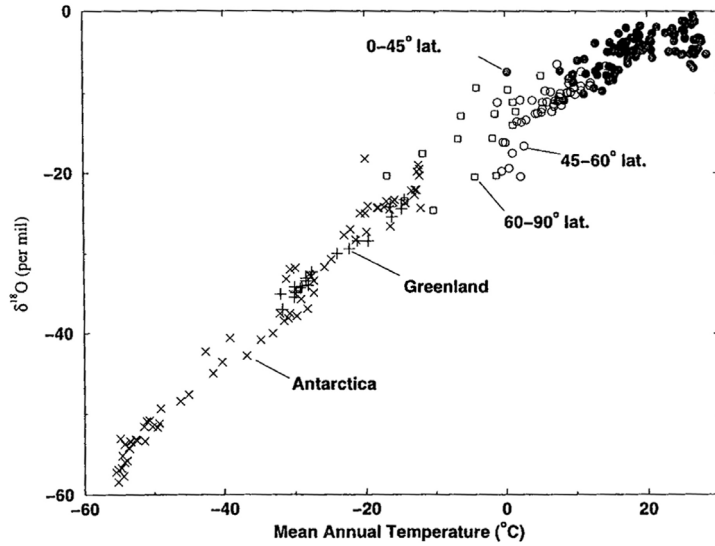


Figure 4. Oxygen isotopic values compared to mean annual temperature originating from ice from various latitudes and ice sheets. Adapted from Dansgaard (1964).

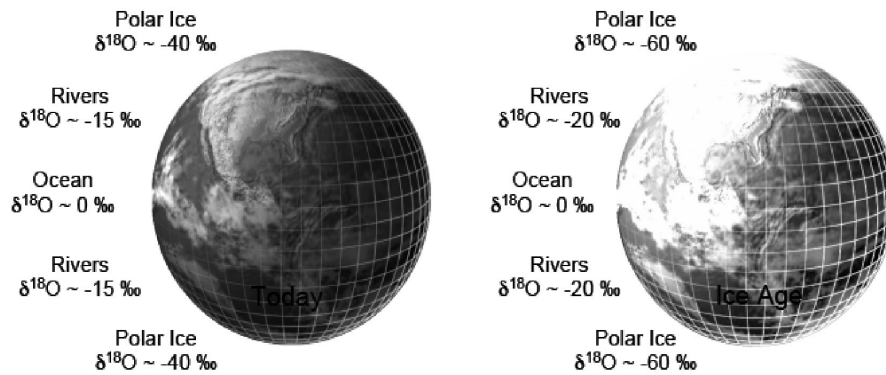


Figure 5. The figure on the left shows the average precipitation at various latitudes during present day and while on the right is for the last glacial maximum.

Effect of ice volume on $\delta^{18}\text{O}$ in seawater

During precipitation as snow or rain, ‘heavy water’ (water with enriched in ^{18}O) tends to precipitate out first, leaving the residual water vapor in the atmosphere to become more enriched in light water (water enriched in ^{16}O). With continued precipitation, the remaining water vapor continues to become enriched in ^{16}O . The result is that water vapor with the light isotope of oxygen (^{16}O) is preferentially transported to the poles from the equator – and there stored as ice. The snow and ice depleted in ^{18}O that falls at high latitudes results in the glacial ice to contain extremely negative $\delta^{18}\text{O}$ values (Figure 4). Additionally, during colder time intervals, such as during the Last Glacial Maximum, precipitation tended to have lower $\delta^{18}\text{O}$ values than today at a given latitude, resulting in even lighter isotopic value of the ice (Figure 5).

As the world’s glaciers grow in volume, ^{18}O values of seawater become larger (more ^{16}O stored in ice) (Figure 6), therefore, $\delta\omega$ of seawater now becomes a register of the size of the global ice sheets. During glacial time, as ice sheets grew (and are enriched in ^{16}O), sea level dropped, and ocean water becomes relatively enriched in ^{18}O . During deglaciation, melt water returned the ^{16}O -depleted water to the ocean, the ocean became less enriched in ^{18}O as sea level rose (Figure 7).

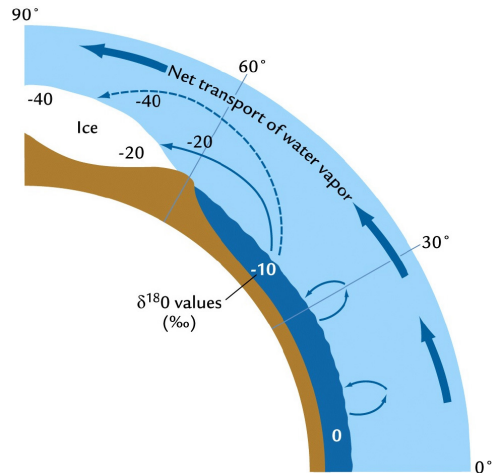


Figure 6. Changes in $\delta^{18}\text{O}$ values during transport are shown as water vapor and precipitation as snow at high latitudes.

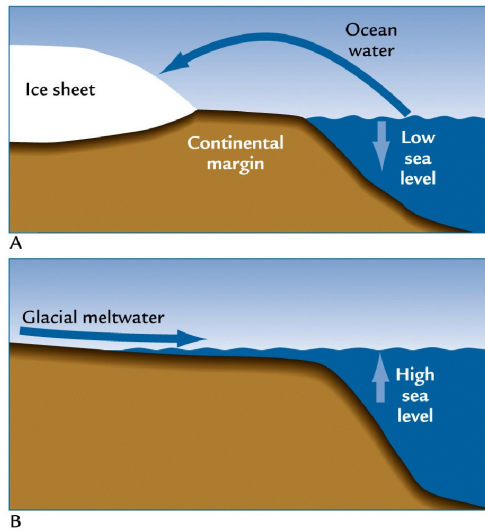


Figure 7. During times of increased ice volume, the oceans become enriched in ^{18}O , resulting in the $\delta^{18}\text{O}$ value of the ocean to increase. As the ice sheets melt, the runoff, which is enriched in ^{16}O , increases the $\delta^{18}\text{O}$ value of the ocean as sea level rises.

Oxygen isotope paleothermometry

Urey (1947) showed that the temperature at which CaCO_3 precipitates affects the ratio of the $\delta^{18}\text{O}$ in the carbonate and that in thermodynamic equilibrium, calcite and seawater differ systematically in $^{18}\text{O}/^{16}\text{O}$ ratios as a function of temperature. Since then, the temperature dependence of $\delta^{18}\text{O}$ in calcite in equilibrium with water has been determined and refined (Equations 2-4) (e.g., Epstein et al., 1953, Shackleton, 1974).

$$T (^{\circ}\text{C}) = 16.5 - 4.3 (\delta_c - \delta_w) + 0.14 (\delta_c - \delta_w)^2 \quad \text{Equation 2}$$

From Epstein et al. (1953)

$\delta_c = \delta^{18}\text{O}$ of carbonate; $\delta_w = \delta^{18}\text{O}$ of water (both relative to PDB).

$$T (^{\circ}\text{C}) = 16.9 - 4.2 * (\delta^{18}\text{O} - \delta^{18}\text{O}_{\text{water}}) + 0.1 * (\delta^{18}\text{O}_{\text{CaCO}_3} - \delta^{18}\text{O}_{\text{water}})^2 \quad \text{Equation 3}$$

An alternate form of the expression is:

$$\Delta\delta^{18}\text{O}_c = \Delta\delta^{18}\text{O}_w - 0.23 \Delta T \quad \text{Equation 4}$$

This relationship allows the paleoclimatologist to determine the temperature of the seawater at the time when the foraminifers lived.

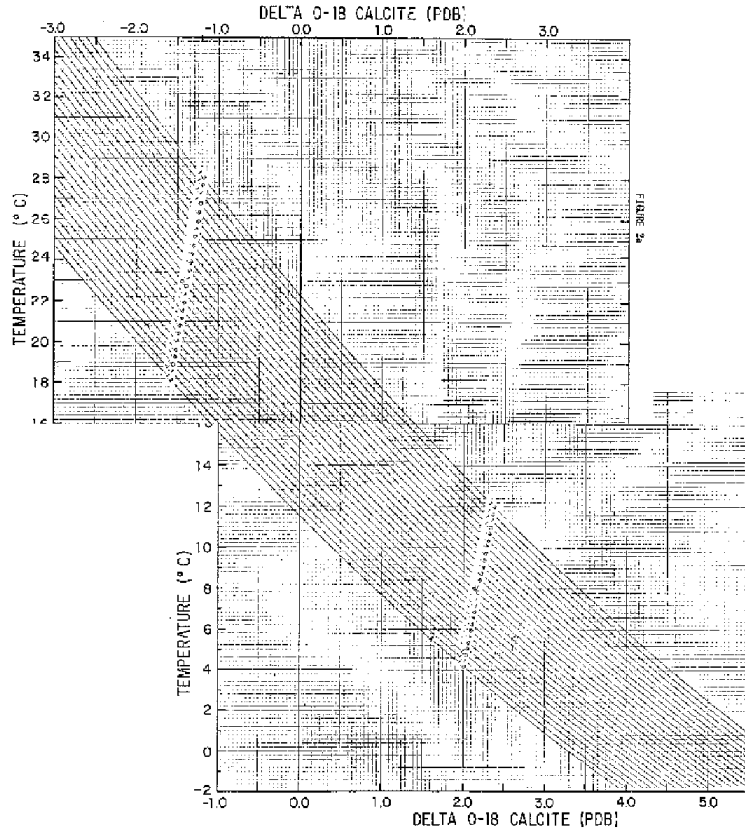


Figure 8. Temperature and $\delta^{18}\text{O}$ relationship from Epstein et al. (1953).

The $\delta^{18}\text{O}$ recorders: Foraminifers

Benthic foraminifera that live in the deep oceans are insulated from large seasonal and geographical variations in temperature and salinity. This makes them more reliable to depict global temperature trends and to calculate changes in average seawater $\delta^{18}\text{O}$ than planktonic foraminifers. In contrast, planktonic foraminifers live at different depths in the water column, which results in a larger uncertainty in estimating ice volume owing to the wider temperature range the upper portion of the ocean contains. Studies have divided planktonic foraminifers into three groups according to their preferred water depths: surface dwellers that live in the surface mixed layer (0-60 m), mid-dwellers that live within the thermocline (60-200 m), and deep dwellers (200+ m).

Intraspecies isotopic offsets of foraminiferal species

Oxygen isotopic values obtained from foraminiferal tests have been shown to vary among species due to intraspecies offsets, which complicates developing oceanic and ice volume reconstructions from these records. These offsets are the result of microhabitat preferences (carbonate precipitation in isotopically distinct environments) and vital effects (species specific metabolic variation in isotopic fractionation) (Katz et al., 2003). Benthic foraminifers often have a consistent offset from each other and from calcite precipitated in equilibrium with the surrounding water, which have been determined for a number of species (e.g., Duplessy et al., 1970; Shackleton, 1974; Belanger et al., 1981; Graham et al., 1981). For example, *Uvigerina* spp. secrete their test in equilibrium with seawater. In contrast, *Cibicidoides* spp. fractionates calcium carbonate out of equilibrium with respect to seawater. However, the offset for *Cibicidoides* spp. has been determined to be constant (+0.64‰) both spatially and temporally. Additionally, as they are epifaunal, and plentiful in most of the deep ocean basins, they are often the preferred benthic foraminiferal species for using for stable isotope analysis. Planktonic foraminifers, in addition to their spatial variability in the water column, also exhibit vital effects, which are enhanced by whether they possess symbionts (blue green algae). Studies have calibrated the species offsets for extant species as well as species that extend back in the Miocene.

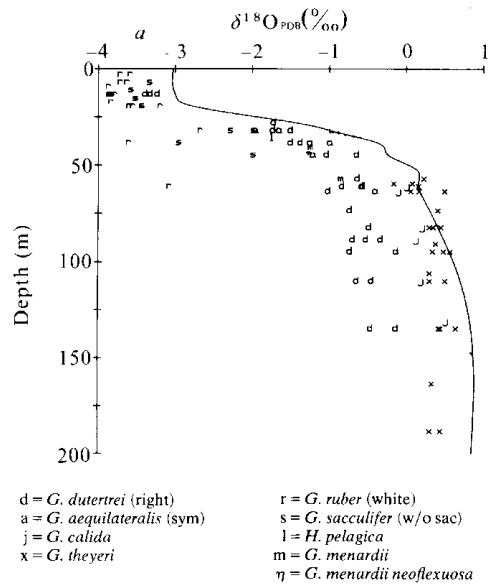


Figure 9. Oxygen isotopic composition of various size fractions of planktonic foraminifers as a function of depth. The solid line is the calculate equilibrium CaCO_3 $\delta^{18}\text{O}$ variation. From Fairbanks et al., 1982.

The oxygen isotopic record of the Cenozoic

One of the great achievements in paleoceanography of the past 30 years has been the development of deep-sea $\delta^{18}\text{O}$ records (Emiliani, 1955; Shackleton and Opdyke, 1973; Shackleton and Kennett, 1975; Miller et al., 1987; Zachos et al., 2001) (Figures 10-13). Although these records are controlled by both deep-sea temperature and ice volume, they recorded first-order changes in climate during the Cenozoic and late Cretaceous. Because of the temperature component inherent in $\delta^{18}\text{O}$ records, methods have been developed in an attempt to isolate the ice volume signal. One method used paired deep-sea benthic and surface dwelling planktonic foraminifers from western tropical warm pools. Shackleton and Opdyke (1973) first studied planktonic and benthic foraminiferal $\delta^{18}\text{O}$ in a core from the western tropical Pacific, a region with minimal season temperature change today (28°C), showing that the two records co-varied by 1.2‰ (Figure 11).

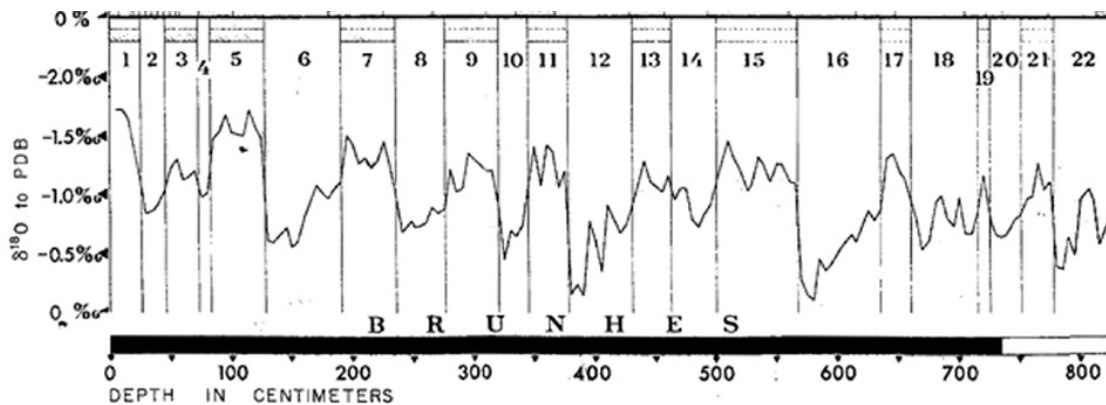


Figure 10. Vema 28-238 $\delta^{18}\text{O}$ record of planktonic foraminifers going back through MIS 21 or about 800 ka. Shackleton and Opdyke (1973)

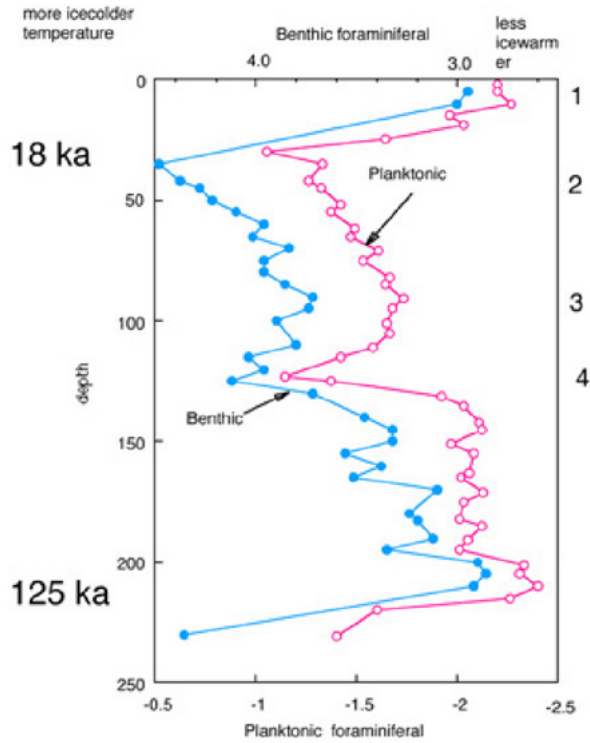


Figure 11. Paired benthic and planktonic foraminiferal $\delta^{18}\text{O}$ records from Vema Core 28-238. The planktonic foraminiferal $\delta^{18}\text{O}$ values show a 1.2-1.3 ‰ amplitude, while the benthic foraminiferal $\delta^{18}\text{O}$ values show a 1.75 ‰ change. Modified from Shackleton and Opdyke (1973).

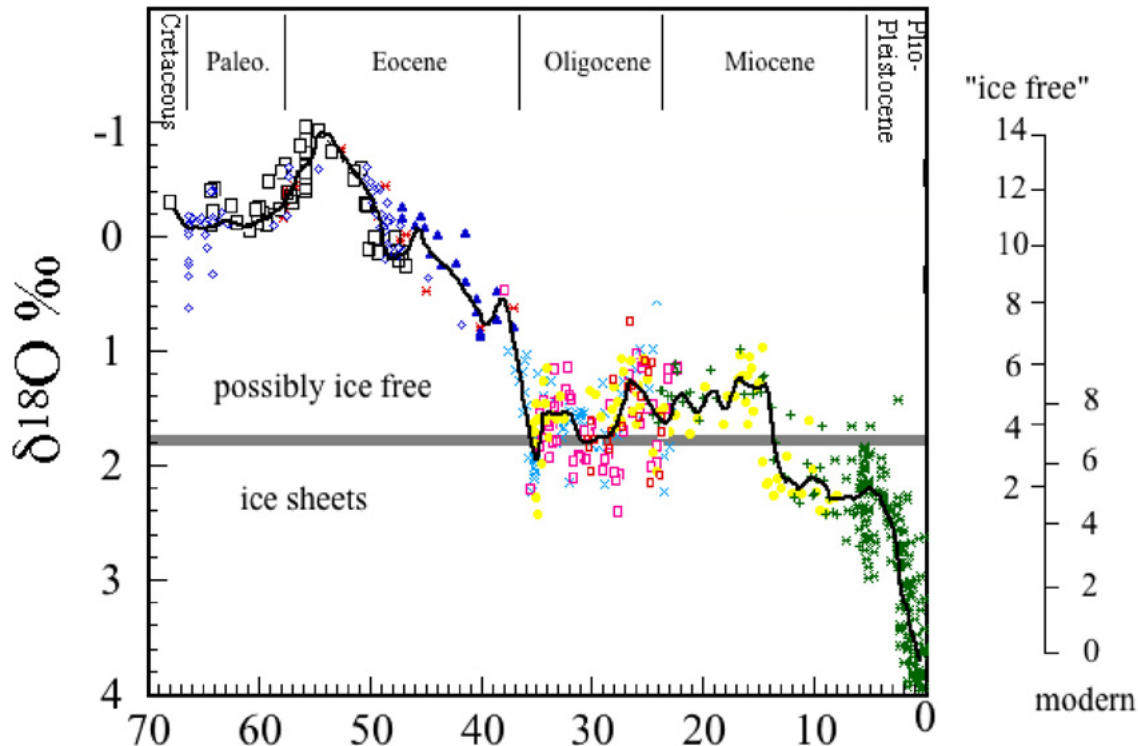


Figure 12. The Cenozoic $\delta^{18}\text{O}$ record modified from Miller et al. (1987). Values greater than 1.8‰, shown by the solid line, are times with some ice volume present. On the right are bottom water temperature estimates for an “ice free” world and for modern-day.

They concluded that this covariance meant that the “ice volume signal” is about 1.2 ‰ as they assumed that the SST’s in these warm pools would have varied little between the last glacial maximum and today. However, the

assumption of constant equatorial sea-surface temperatures (SST's) has been challenged and ice volume estimates using this method represent a maximum value (Guilderson et al., 1994).

Nevertheless, Cenozoic $\delta^{18}\text{O}$ records from deep-sea sites have been used as a proxy for ice-volume changes for times when large ice sheets were thought to have existed (Miller et al., 1985; 1987; 1991; Wright and Miller, 1992; Zachos et al., 2001). During the past three decades, new studies have repeatedly moved back the timing of the first significant continental ice sheets to ever older and warmer periods in the Cenozoic. Stable isotope studies in the 1970's (e.g., Shackleton and Kennett, 1975) suggested that low $\delta^{18}\text{O}$ values before the middle Miocene prohibited the development of large continental ice sheets. Subsequent studies (e.g., Miller et al., 1985; 1987; 1991) identified large ($>0.6\text{‰}$) $\delta^{18}\text{O}$ increases with maximum values $>2.0\text{‰}$, that co-vary in both the benthic and planktonic foraminiferal records and concluded that they represent the presence of intermittent large continental ice sheets from the middle Miocene through the Oligocene. These were subsequently defined as isotopic zones and were correlated to sequence boundaries identified from shallow water stratigraphic sections, confirming that these increases are due at least in part to glacioeustatic changes (Miller et al., 1991; Wright and Miller, 1992). Miller et al. (1987) also determined that $\delta^{18}\text{O}$ values $>1.8\text{‰}$ represent the presence of significant ice. This is based on that higher values in an ice free world would result in bottom waters colder than today, which is not compatible with our understanding of ice sheet development.

Although the timing of Oligocene through Miocene deep-sea $\delta^{18}\text{O}$ increases are relatively well constrained, constraining ice volume amplitudes based solely on $\delta^{18}\text{O}$ records alone has not been possible. While the large and rapid $\delta^{18}\text{O}$ variations that define the isotopic events must reflect some ice growth and decay, the temperature component needs to be evaluated for ice volume to be determined. Comparisons of benthic and western tropical planktonic foraminiferal isotopic records from the Cenozoic made assumptions that warm pools in the tropics remain constant between glacial and interglacial times. However, since this has been shown not to be true for the late Pleistocene (Guilderson et al., 1994), it should not be assumed for the pre-Quaternary times either. Therefore, any estimate of ice volume changes using this method should also be considered as a maximum value as in Quaternary records (Wade and Palike, 2004).

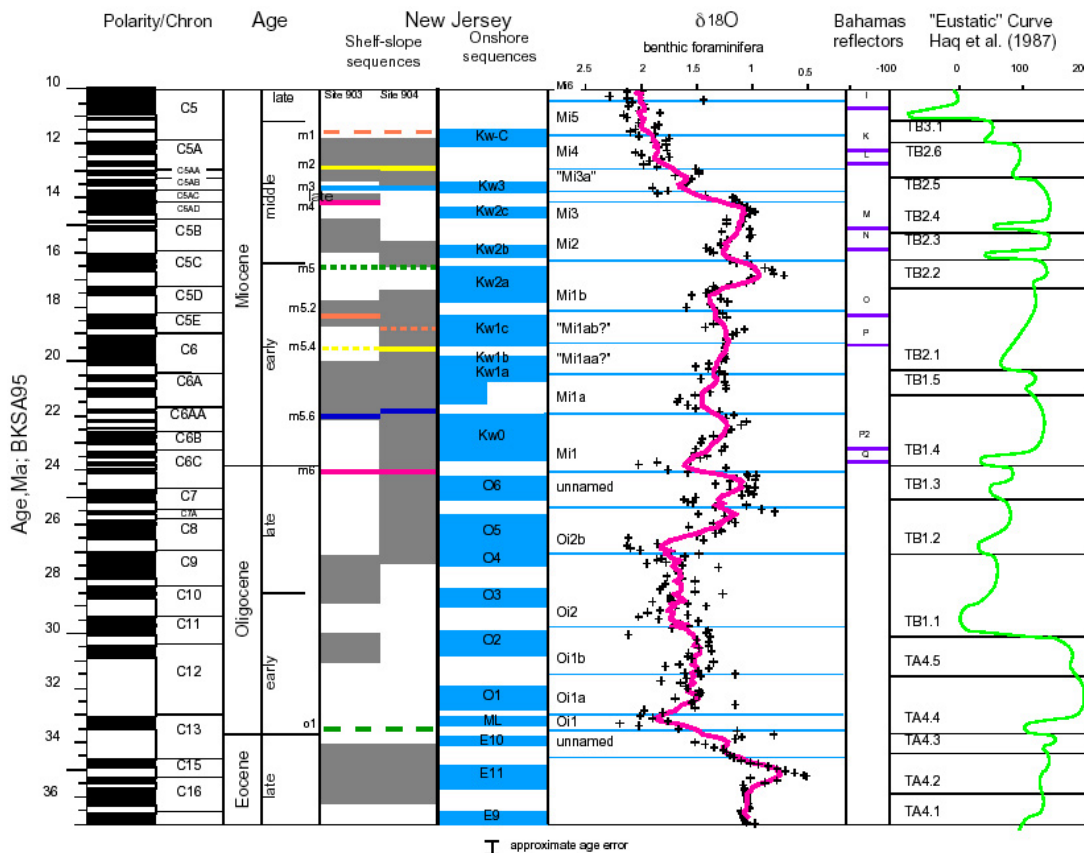


Figure 13. Summary figure from Miller et al. (1998) showing the good agreement between the sequence boundary development from both shallow and slope stratigraphy and $\delta^{18}\text{O}$ events identified from deep-sea records. This is a revised comparison of Oligocene-Miocene slope sequences, onshore sequences, oxygen isotopes, Bahamian reflections (Eberli et al., 1997), and the inferred eustatic record of Haq et al. (1987).

Isotopic and stratigraphic evidence indicates that during the middle and late Eocene, small ephemeral ice sheets existed (Browning et al., 1996; Miller et al., 1998; Pekar et al., 2005). These ice sheets presumably existed in the interior of the continent, residing on the plateaus, with ice volume generally being less than 60% of the present-day East Antarctic Ice Sheet (EAIS) (Miller et al., 1998; Pekar et al., 2005; Miller et al., 2005).

Dialing out the temperature signal in $\delta^{18}\text{O}$ records: Mg/Ca ratios (based on Lear, in press)

Up until the late 1990's, estimates of Cenozoic ice volume and water temperature were derived primarily from $\delta^{18}\text{O}$ composition of benthic and planktonic foraminiferal tests. However, because the $\delta^{18}\text{O}$ values are a function of the temperature during calcification and the $\delta^{18}\text{O}$ value of the seawater, the goal has been to develop a method that can isolate the temperature signals so we can evaluate ice volume. During the past ten years, great strides have been made in the development of using Mg/Ca ratios as a means to constrain water temperature both during the Quaternary and older periods (Martin et al., 1999; Billups and Schrag 2002; 2003; Lear et al., 2000; 2004). This is supported by the general agreement in temperature estimates between organic biomarkers (e.g., alkenone saturation) in sediments and Mg/Ca ratios in planktonic foraminiferal tests (Lea et al., 2002).

Experiments have shown that the partition coefficient of Mg^{2+} into inorganic calcite increases with increasing temperatures. Subsequent studies have shown that a positive Mg/Ca temperature relationship in biogenic calcite exists based on both empirical and culture experiments (Dwyer et al., 1995; Nürnberg et al., 1996; Rosenthal et al., 1997; Lea et al., 1999; Elderfield and Ganssen, 2000; Anand et al., 2003). However, the magnitude of the foraminiferal Mg/Ca-temperature relationship is about twice that observed in inorganic calcite suggesting that a biological influence exists on this calcification process (Rosenthal et al., 1997). This influence is also indicated by different Mg/Ca ratios measured between species living at the same temperature.

Calibrating Mg/Ca to Temperature

Calibration studies of Mg/Ca to temperature typically use recent or live foraminifers and water temperature data from where they live. For benthic foraminifers, tests are collected from top core samples while planktonic tows can be used to sample planktonic foraminifers. Additionally, culture experiments carried out in laboratories using foraminifers have also been performed to develop data for calibrating Mg/Ca to temperature. A number of Mg/Ca temperature calibrations exist for planktonic foraminifers (e.g., Nürnberg et al., 1996; Elderfield and Ganssen, 2000; Lea et al., 1999). Calibrations for benthic foraminiferal species are more difficult to obtain as single species often inhabit limited water depth and hence temperature ranges. Because calibrations are based on modern specimens, species-specific calibrations decrease as we go further back into the Cenozoic. This is especially true for planktonic foraminifera, which tend to evolve faster than benthic foraminifera. Benthic foraminiferal species often have longer temporal ranges, with a number of modern forms extending back into the Neogene and Paleogene.

Thermodynamic considerations suggest that Mg/Ca-temperature relationships should be described by an exponential fit (e.g., Rosenthal et al., 1997) (Figure 14). Most Mg/Ca-temperature calibrations therefore follow the form described by equation 5, where A is an exponent that reflects the temperature-sensitivity of the foraminiferal species; the higher the exponent, the greater the absolute change in Mg/Ca per degree change in temperature. The consistency of the Mg/Ca-temperature sensitivity in both benthic and planktonic foraminifera from a wide variety of oceanic and artificial laboratory settings gives us confidence in applying this proxy to the fossil record.

$$\text{Mg/Ca}_{\text{FORAM}} = B \exp(A \times \text{Temperature})$$

Equation 5

A Saturation State Effect on Benthic Foraminiferal Mg/Ca

The degree of carbonate saturation appears to exert a secondary control on Mg/Ca ratios (Martin et al., 2002). Although typically small (a recent estimate of the sensitivity of carbonate ion saturation on Mg/Ca is 0.0086 mmol/mol/mmol/kg, (Elderfield et al., 2006)) this effect must be taken into account when interpreting down-core and site-to-site Mg/Ca records where a significant change or difference in seawater saturation state is suspected.

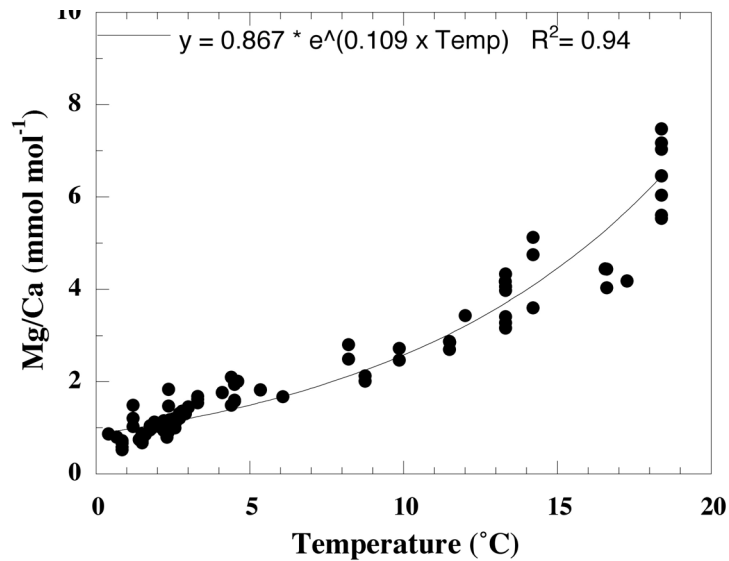


Figure 14. From Lear et al., (2002) showing relationship between Mg/Ca and bottom water temperatures from the benthic foraminifera *Cibicidoides* spp.

Temporal variations in seawater Mg/Ca

The degree of substitution of Mg^{2+} in the calcite lattice is dependent on the partition coefficient, D_{Mg} , specific to the calcifying organism, and the concentration of magnesium relative to calcium in the fluid used by the organism. The amount of Mg^{2+} relative to Ca^{2+} is more or less invariant within the ocean today, however, for Cenozoic studies, the Mg/Ca temperature calibration should include past variations in seawater Mg/Ca (equation 6).

$$\text{Mg/Ca}_{\text{FORAM}} = \frac{(\text{Mg/Ca})_{\text{SW-T}}}{(\text{Mg/Ca})_{\text{SW-0}}} \times B \exp(A \times \text{Temperature}) \quad \text{Equation 6}$$

While no direct records of ancient seawater Mg/Ca ratios exists, studies have suggested that $[\text{Mg}^{2+}]$ and $[\text{Ca}^{2+}]$ in seawater changed slowly owing to long residence times of Mg^{2+} and Ca^{2+} in seawater (~ 1 m.y. and 10 m.y. respectively) (Broecker and Peng, 1982). This indicates that any change in the seawater Mg/Ca ratio must have occurred extremely slowly. This means that obtaining records from short time records ($<10^6$ yrs) within the Cenozoic, or when comparing records from different locations but of the same age, the changes in Mg/Ca is not significant. Therefore, even if we were uncertain on the degree of Mg/Ca change in the seawater through the Cenozoic, we can still constrain relative temperature changes with a high degree of certainty, even though some uncertainty may exist regarding the absolute temperature estimates.

Three lines of evidence have been developed to provide estimates how seawater Mg/Ca has varied throughout the Cenozoic. The first uses the composition of fluid inclusions caught up in evaporite minerals. This method suggests that at around 50 Ma, seawater Mg/Ca was likely between 2.5 and 3.5 mol/mol (e.g., Lowenstein et al., 2001). The second line of evidence comes from biogenic carbonate Mg/Ca ratios, such as the Mg/Ca of foraminifera that lived in the greenhouse world of the early Cenozoic. With zero (or near zero) continental ice volume, we can use benthic foraminiferal oxygen isotope ratios to calculate bottom water temperatures for these times. We can then use equation 6 to calculate seawater Mg/Ca, which suggests that during the early Cenozoic, seawater Mg/Ca was between 3 and 5 mol/mol. The final (and least constrained) line of evidence is through modeling the processes that may change the concentrations of Mg^{2+} and Ca^{2+} in the ocean and include hydrothermal alteration of basaltic crust, calcification of marine organisms, dolomite formation, and the flux of Mg^{2+} and Ca^{2+} ions brought to the ocean by rivers. Predicted seawater ratios vary between models, from around 1.6 mol/mol (Demicco et al., 2005) to around 3.9 mol/mol (Wilkinson and Algeo, 1989) at ~ 50 Ma. Estimates of seawater Mg/Ca using the different techniques converge towards the present day known value of 5.2 mol/mol, so that uncertainties in calculating absolute temperatures and seawater $\delta^{18}\text{O}$ are reduced in younger sediments.

Foraminiferal sample preparation and analysis

In obtaining Mg/Ca ratio measurements from foraminifers, a rigorous cleaning method has been developed to remove contaminants from the test. Most methods are a variant of the cleaning methods describe by Bole and Keigwin (1985/86), which comprise of a number of steps to remove various types of contaminants. This includes removing clays,

organics and oxide coatings. To ascertain if the contaminants have been removed satisfactorily from the tests, iron, titanium, or aluminum should also be analyzed to provide a basis for removing or correcting contaminated samples. For example, Barker et al. (2003) used Fe/Mg ratios greater than 0.1 mol/mol as rejection criteria where clays were believed to be the prime contaminant.

Preservation of foraminiferal calcite

Pos-mortem diagenetic processes can have a detrimental effect on the Mg/Ca ratio signal in foraminiferal calcite. For example, partial dissolution of a foraminiferal test will cause both a decrease in the test mass, and also the average Mg/Ca of the remaining calcite. In some cases this relationship can be used to correct for the effects of dissolution on foraminiferal Mg/Ca (Rosenthal and Lohmann, 2002). Planktonic foraminifera have a greater risk of dissolution owing to the large change in the chemistry between surface and deep water, with the latter typically being more corrosive to calcite. Recrystallization of foraminiferal calcite and the subsequent alteration on the geochemistry of the test, is always a problem not only for Mg/Ca, but also $\delta^{18}\text{O}$ records. Recrystallization process are enhanced in carbonate-rich sediments, with foraminifera obtained from clay-rich sediments are more likely to retain their original microstructure and geochemistry (e.g., Pearson et al., 2001).

Cenozoic glaciation based on paired deep-sea $\delta^{18}\text{O}$ and Mg/Ca ratio records

Mg/Ca ratios have provided a means to isolate seawater temperatures permitting determination of the $\delta^{18}\text{O}$ of seawater ($\delta\omega$) and therefore provide constraints on ice volume. Paired low-resolution benthic foraminiferal Mg/Ca ratio and $\delta^{18}\text{O}$ records depict a long-term cooling trend since the early Eocene (Lear et al., 2000) (Figure 15). Additionally, three significant periods of increased ice volume occurred during the Cenozoic: the earliest Oligocene, the middle Miocene, and the Plio-Pleistocene. However, while Mg/Ca ratios indicate that both the middle Miocene and Plio-Pleistocene are associated with overall cooling of the deep-sea, Mg/Ca ratios do not show any significant bottom water cooling during the early Oligocene (Lear et al., 2000; 2004). This appears to be inconsistent with ideas of ice sheet development and its effects on bottom water temperature. It would also result in the entire isotopic change observed in the $\delta^{18}\text{O}$ records across the Oi-1 event (as defined by Miller et al., 1991) to be due entirely to ice volume increase. This is unrealistic as the ice sheet would have to be more than twice the size of the present-day ice sheet (Coxall et al., 2005).

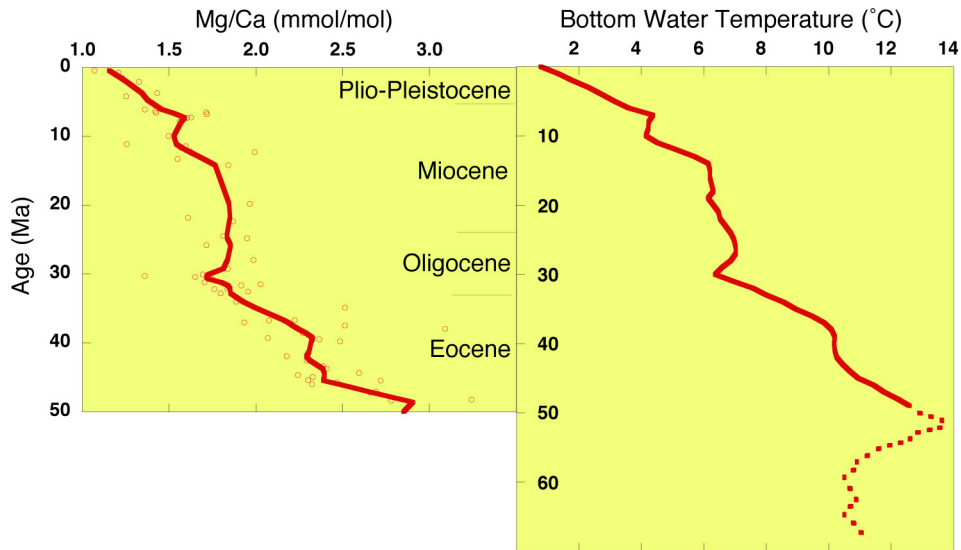


Figure 15. Mg/Ca ratios and the derived bottom water temperatures from Lear et al. (2000).

However, Lear et al. (2004) provided a possible explanation for the absence of temperature change across the one of the largest climate changes of the Cenozoic. The Oi-1 event is coincident with a dramatic increase in seawater carbonate saturation state. This is indicated by increasing carbonate content of deep-sea sediments and a 1.2 km deepening of the calcite compensation depth (Coxall et al., 2005; Rea and Lyle, 2005). In studies using core-top benthic foraminifera from sites very close to saturation with respect to calcite, the Mg/Ca ratios have lower ratios than expected (Martin et al., 2002). Therefore, Lear et al. (2004) suggested that the increased carbonate saturation state affected the Mg/Ca ratios in their deep-sea record from ODP 1218, causing an “apparent” warming of $\sim 2^\circ\text{C}$. Nevertheless, the temperature history across Oi-1 therefore remains poorly constrained.

Cenozoic glacio-eustatic sea level change

Conversion of seawater $\delta^{18}\text{O}$ to ice volume and the resulting sea-level change necessitates estimates of the precipitation and evaporation history (the salinity effect) of the water mass as well as the isotopic values of the ice sheets. The “salinity effect” can vary deep-water $\delta^{18}\text{O}$ values by several tenths of a per mil, which is equivalent to 10 to 30 meters of apparent sea level (See the Pekar and Kominz chapter in this book). By placing constraints on the type of the water mass (e.g., estimating water depths and using both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ isotopes) and then comparing it to modern-day analogues, the salinity of the water mass can be constrained (Pekar et al., 2002). Evaluating the amplitude of ice volume also requires an estimate of isotopic value of the ice. Fairbanks (1978) assumed an isotopic composition of the ice of -42‰ providing a calibration for Pleistocene ice of $0.11\text{‰}/10$ meters sea level. However, in a temperature ice sheet, such as that probably existed during the Oligocene and Miocene, a smaller calibration may be more reasonable ($0.09\text{‰}/10\text{-m}$ sea level) (DeConto and Pollard, 2003). For warmer periods, ever smaller calibrations may be necessary ($0.8\text{‰}/10$ m sea level change, Pekar et al. [2005]).

Lear et al. (2004) developed a continuous and high-resolution paired $\delta^{18}\text{O}$ and Mg/Ca ratio record from ODP Site 1218 (Lear et al., 2004). These records extend from the late middle Eocene to early Miocene (42 to 18 Ma). Lear et al. (2004) combined the temperature estimates from the Mg/Ca ratio records with $\delta^{18}\text{O}$ records to calculate variations in ice volume and therefore provide a means to evaluate ice volume. They estimated maximum ice volume during the Oligocene and early Miocene of up to 150% of the present-day East Antarctic Ice Sheet or equivalent to 90-meters of sea level if all of the ice melted. This is in good agreement with the eustatic estimates of 80 ± 15 meters from backstripped stratigraphy of Kominz and Pekar (2001). Both deep-sea and stratigraphic records also indicate that once the continental ice sheet developed at the base of the Oligocene, ice volume never diminished to the small ephemeral ice sheet of the Eocene (see Kominz and Pekar chapter in this book).

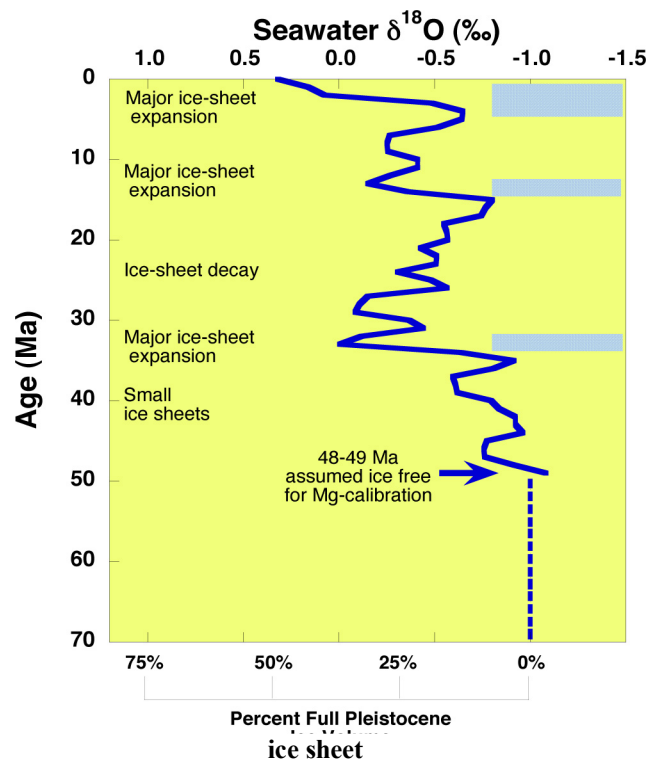


Figure 16. Estimates of the isotopic value of seawater derived from paired Mg/Ca ratio and $\delta^{18}\text{O}$ records (Lear et al., 2000) showing the three large increases in ice volume during the earliest Oligocene, mid Miocene, and Plio-Pleistocene.

Lear et al. (2004) also indicate that ice volume was greatest during the earliest Oligocene (Oi-1 event), during the “mid” Oligocene (28-26 Ma) and during the early Miocene isotopic events. It also appears that ice volume during the Oi-1 event may have not been as large as the other two intervals of maximum ice volume. This is also in good agreement with ice volume estimates from calibrated isotopic records of Pekar and Christie-Blick (in press) that suggest that the greatest ice volume occurred between 28 and 27 Ma and during isotopic events during the early Miocene (Pekar and DeConto, 2006) (see Kominz and Pekar chapter in this book). The $\delta\omega$ values also indicate that the Antarctic ice

sheet varied between 50 and 100% of its maximum Oligocene mass (150% of the present-day EAIS) and is in excellent agreement with ice volume estimates from Pekar and Christie-Blick (in press).

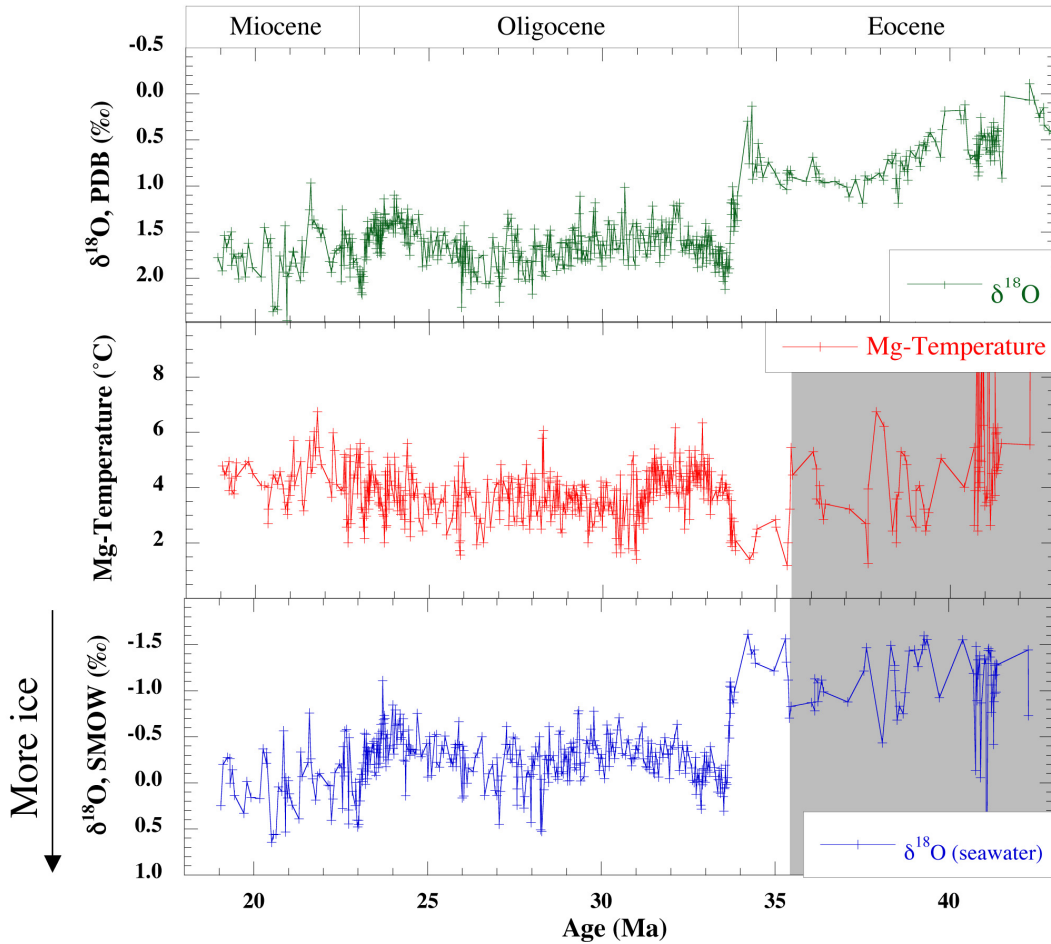


Figure 17. The high-resolution records from ODP Site 1218 (Lear et al., 2004). These records indicate that after the onset of large ice sheets in Antarctica at the Eocene-Oligocene climate transition, the ice sheet never returned to the small ice sheets of the Eocene.

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